THE FEASIBILITY OF A CONTINUOUS HYDROGENATION OF COTTONSEED OIL IN A PIPE SYSTEM

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THE FEASIBILITY OF A CONTINUOUS HYDROGENATION OF COTTONSEED OIL IN A PIPE SYSTEM

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ABSTRACT

An investigation was made to study the influence of rate of flow of cottonseed oil, reduced nickel catalyst, and hydrogen, excess hydrogen, catalyst concentration, temperature, and, with the continuous process, the difference in the process of hydrogenation itself on the rate of hydrogenation and on the selectivity of the reaction in the continuous process of hydrogenation in order to determine the optimum conditions under which the nature of the product obtained by this method would be similar to that of the product obtained by the batch process.

In a pipe system consisting of forty-seven feet of $1\frac{1}{2}$ inch steel pipe, a positive displacement pump, hydrogen jet nozzle, electrical resistance heating elements, surge tank, rotameter, and the auxiliary equipment necessary to load the system, and consequently filter the hydrogenated oil, it was possible to hydrogenate a circulating cottonseed oil stream at flow rates ranging from 4.2 GPM to 8.8 GPM into a hardened product. The reaction, in some cases, produced a selectively hydrogenated oil comparable to that obtained by the batch method of hydrogenation.

The system was charged with 75 pounds of bleached, refined, and,

in some runs, winterized cottonseed oil. The circulating oil was pre-heated to a temperature of 350 °F., a pre-determined amount of reduced nickel catalyst added, and, after the system had been regulated to the desired operating conditions, hydrogen was admitted through a brass nozzle into the process piping. The length of the runs was two hours in most cases.

Upon completion of the hydrogenation, the oil was freed of the nickel catalyst by the use of a plate and frame filter. The resulting products were subjected to iodine value, thiocyanogen value, and Wiley melting point determinations in accordance with the official methods of the American Oil Chemist Society. Also, iodine values were obtained for the samples that were taken at fifteen minute intervals during the various runs. From the analytical data obtained, knowledge of the rate of hydrogenation and the degree of selectivity of the reaction was obtained.

From this investigation, it was concluded that it is possible to obtain a product from a continuous process that is similar to an all-hydrogenated product from a batch process. The selective reaction appeared to depend not only on the temperature, catalyst concentration, pressure, and quantity of hydrogen used, but, also on the rate of flow, method of the hydrogenation process itself, and the relative amounts of major constituents in the original oil.

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INTRODUCTION

The edible fat industries in the world today demand that products such as margarine and vegetable shortening possess as little susceptibility to oxidation (and therefore rancidity) as possible and at the same time possess relatively low melting points. The presence of linoleic glyceride is undesirable in these products, since it tends to become oxidized and rancid. Likewise, stearic glyceride is undesirable and should be minimized because its melting point is too high to be tolerated to any large extent in edible products. Therefore, a process of converting the linolein into olein with the formation of relatively little stearin is of great advantage to the above mentioned industries. The batch process of hydrogenation of vegetable oils answers this purpose on account of its preferential or selective conversion of linolein into olein before there is any material increase in the stearin and, consequently, has been adopted almost entirely by the edible fat industries.

Comparison of the batch process and continuous process shows that the latter has many advantages over the former from the point of view of operations, but, according to the few investigators of the continuous process, it is not suited for wide industrial application on account of its non-selective character. Although a considerable

amount of work has been done to study the effect of the operating conditions on the degree of selectivity in the batch process, a detailed study of the literature reveals that no extensive investigation has been done as to the effect of operating conditions on the degree of selectivity in the continuous process.

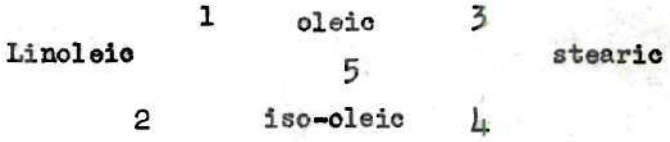
This investigation is an attempt to study the influence of rate of flow of the oil, catalyst, and hydrogen, excess hydrogen, amount of catalyst, temperature, and, with the continuous process, the difference in the process of hydrogenation itself on the rate of hydrogenation and on the selectivity in the continuous process of hydrogenation in order to determine the optimum conditions under which the nature of the product obtained by this method will be similar to that of the product obtained by the batch process.

THEORY OF THE HYDROGENATION OF EDIBLE OILS

To produce fats of higher melting points from edible liquid oils, and to reduce their tendency toward oxidation, it is customary to hydrogenate the oils partially and selectively to a degree dependent on the uses to which the hydrogenated product is to be put.

Definition of Selectivity

Jamieson[1] defines selectivity in this case as the reduction, to a considerable extent, of the more unsaturated glycerides before the less unsaturated ones begin to react. He says that in partial hydrogenation some stearic glycerides are formed along with considerable quantities of the so-called iso-oleic and normal oleic glycerides from the reduction of linoleic glyceride to the extent dependent upon the degree of selectivity of the reaction. Bailey[2] represented the probable course of the principal concurrent and consecutive reactions as follows:



The term "oleic" refers to normal oleic glycerides (ethylenic linkage at the 9-10 position in the C_{18} chain) and "iso-oleic" to the high melting trans-isomers which includes the positional and geometrical isomers of the normal oleic glycerides. "Linoleic" refers to all other diethenoid glycerides. The overall reaction is termed <u>selective</u> or <u>preferential</u> when the velocity constants for reactions 1 and 2 are large in relation to those for reactions 3 and 4. He says that high

selectivity is invariably accompanied by a relatively large production of iso-oleic glycerides from reactions 2 and 5. Bailey[3] points out that the hydrogenation of edible oils should result principally in the reduction of linoleic glycerides to oleic glycerides rather than oleic to stearic, and that the formation of iso-oleic content should be minimized because of its higher melting point.

Advantages and Disadvantages of Selective Hydrogenation

In the hydrogenation process of converting liquid cottonseed oil (containing approximately 23% oleic glyceride and 48% linoleic glyceride and possessing one and two double bonds, respectively, in the C_{18} chains) into and edible hardened product, the advantage of selective hydrogenation lies in the conversion of linoleic to oleic glycerides before there is any material increase in the glycerides of the saturated fatty acid esters. This advantage is somewhat overcome by the fact that the oleic glycerides are not all liquid; thus when cottonseed oil is partially hydrogenated the product is a mixture of several oleins, some of which are solid. The disadvantage of the solid oleins, i.e., the iso-oleins, are their higher melting points (a higher melting point for a hardened fat of a given iodine value), and, also, the crystal structure of the solid iso-oleins, which is usually that of large, soft, waxy plates, tend to affect the appearance and consistency of edible fats in which they may be present. Since the melting point of 9-10 normal oleic glyceride is approximately 15 °C. and iso-oleic approximately 40 °C., the goal of the partial hydrogenation of edible oils into shortening and margarine products is to obtain as high a normal olein content as

possible by converting the less saturated esters to normal olein without the formation of the esters of completely saturated acid and iso-oleic acid. In other words, in the industrial production of hardened oils attempts are made to obtain a fat of the lowest iodine value (and therefore the least unsaturation) compatible with a relatively low melting point.

Mechanics of the Hydrogenation Reaction

Since it is necessary to utilize the selective reaction in the conversion of edible oils into finished fat products for reasons stated previously and since the iso-oleic glyceride content should be minimized due to its relatively high melting point, one might ask: Why are the iso-oleic glycerides produced in the selective reaction? Hilditch[4] answers this question by pointing out that the ethylenic linkages in unsaturated fats such as linoleic glycerides occur at different points in the C_{18} chains; therefore it is easy to understand why the oleic glycerides produced by selective hydrogenation are not all the same and identical with ordinary normal oleic or 9-10 octadecenoic acid. The double bond left may equally well be one of the others. This is probably the chief cause of the occurence of solid iso-oleic glycerides, but there is also another means whereby they are produced during the hydrogenation of the glycerides of oleic acids itself. It has been shown by Moore[5] that in addition to stearic derivatives, esters of elaidic acid (the solid geometrical isomeride of normal oleic glyceride) and other solid positional isomers of normal oleic glyceride among which is the 12-13 octadecenoic ester are produced by what has

been referred to as a continual hydrogenation-dehydrogenation type of reaction. Hydrogenation of an oil involves the following sequence of operations, according to Bailey[2]:

1. Solution of hydrogen in the oil
2. Adsorption of dissolved hydrogen on the catalyst
3. Prior or later adsorption of unsaturated oil
4. Reaction to form a nickel-hydrogen-oil complex
5. Decomposition of the complex to yield hydrogenated oil and free nickel
6. Desorption of the hydrogenated oil.

He says that the concentration of hydrogen in the actual reaction zone, i.e., adsorbed on the catalyst, is subject to wide variation, according to the efficiency of hydrogen transfer from the gas to the liquid phase (degree of dispersion in the oil) and the rate at which it is taken up by the reaction as well as the hydrogen pressure in the system.

Adsorption (and reaction) of the active methylene grouping, $-CH=CH-CH_2-CH=CH-$, appears to be fundamentally different from that of an isolated double bond, and, is presumably related to the readiness with which a hydrogen atom may be detached from the central carbon atom[6, 7]. Hydrogenation of a double bond in this group occurs much more readily than hydrogenation of an isolated double bond. However, the relative activities in the two cases are dependent upon the concentration of adsorbed hydrogen and may vary widely according to the conditions of hydrogenation. Therefore, hydrogenation of a double bond in a single group as shown above so as to convert a diethenoid

acid to a monoethenoid acid (linoleic to oleic), is followed by desorption of the monoethenoid acid from the catalyst.

Bailey[2] supports the arguments of the other investigators that the formation of a certain amount of high melting trans-monoethenoid isomers (iso-oleic esters) in the hydrogenation of a fat, such as cottonseed oil, is not only due to a by-product of the hydrogenation of polyethenoid esters, but is also produced during the hydrogenation of pure monoethenoid esters. To a minor degree, migration of double bonds occurs, producing positional isomers, which is the same sort of phenomena referred to previously as a hydrogenation-dehydrogenation type of reaction.

Effect of Operating Variables on Selectivity and Rate of Hydrogenation

Although comparatively little work has been done to study the effects of the operating conditions on the hydrogenation reaction in the continuous process, an extensive amount of work has been done to study the influence of catalyst concentration, pressure, agitation, and temperature in the batch process. The influence of these variables on the rate of hydrogenation and degree of selectivity as reported by investigators of the batch process is as follows:

1. Catalyst - The concentration of catalyst influences both the rate of hydrogenation and the selectivity of the reaction. That the rate is proportional to the amount of catalyst is well established, but, as to its effect on selectivity, there appears to be some disagreement. Moore[8] and co-workers found that an increase in the concentration of catalyst decreases the selectivity while Richardson,

Knuth, and Milligan[9], Hilditch[10] and co-workers have drawn conclusions contradictory to those drawn by Moore. They have observed that an increase in the amount of catalyst increases the selectivity.

2. Pressure - That the hydrogenation rate is accelerated by increasing the pressure is also fully supported. Ellis[11] says that the time to reduce the unsaturation to a certain level is roughly cut in half by doubling the pressure. From the viewpoint of selectivity, Moore[8] has observed that an increase in pressure leads to less selective results which has been confirmed by Waterman[12] and others. Contradictory views have been held by Richardson, Knuth, and Milligan[9].

3. Temperature - There appears to be no controversy regarding the observations that increases in temperature within a certain range (100 °C. to 200 °C.) increase the rate of hydrogenation and the selectivity of the reaction.

4. Agitation - An increase in the degree of agitation has been reported by all investigators, as far as is known, as promoting the hydrogenation reaction. As to selectivity, Moore[8] has observed that an increase in the agitation decreases the selectivity, while several workers maintain that a decrease in agitation decreases selectivity.

In the study of continuous hydrogenation, one more factor is introduced, namely, the difference in the process of hydrogenation. Lush[13] in his study of the progressive hydrogenation of vegetable oils with a fixed catalyst emphasized that the continuous process gives

less selective results than the batch process. Athavale and Jatkar[14] in their investigation of the continuous process are of the opinion that the selectivity depends not on the process but on the nature of the catalyst.

REVIEW OF CONTINUOUS PROCESSES

Because of non-selective results reported by a few investigators, and possibly, because of unpublished results, the data in the literature on continuous hydrogenation of vegetable oils are very meager. Since 1923, the year in which Lush introduced the continuous process in the field of hydrogenation, the investigators of such a process number only a few.

A brief review of the continuous hydrogenation of vegetable oils from 1923 to the present time with a more comprehensive discussion of the patents granted recently will be given.

The advent of the continuous process in 1923 attracted considerable attention. Its development was credited to Lush and Bolton, and it was exploited by The Technical Research Works, Ltd. The catalyst used in this process was in massive form, consisting of nickel turnings, activated on the surface, and enclosed in removable cages. Activation of the catalyst was affected by anodic oxidation and reduction in hydrogen. The oil and hydrogen passed over a series of these catalyst cages, the oil dripping through the catalyst and being continuously in contact with hydrogen. The largest plant built by The Technical Research Works had a capacity of 33,000 pounds per day[15] and hydrogenated to an iodine value of 50. A more detailed description may be obtained from an article by Lush[16] or from the patent[17] granted. Lush found that above a certain minimum rate of flow of oil the hydrogen absorbed per hour is independent of the flow of oil, or in other

words the degree of hydrogenation of the oil as measured by the drop in iodine value is proportional to the speed of the oil passing through the plant. As a result of his studies of this process, Lush emphasized that the continuous process gives less selective results than the batch process. It is for this reason, together with the relatively small capacity of the plant, that this process has not been universally adopted.

Hilditch[18] and co-workers reached similar conclusions as to degree of selectivity from their study of the Lush principle of the progressive hydrogenation of cottonseed oil. Hilditch did not give rates of flow of the oil, but his results indicate that the olein to stearin reaction predominates.

Later, Athavale and Jatkar,[14] who have made a systematic study of the continuous process with cottonseed oil at rates of flow ranging from about forty grams per hour to slightly over two hundred grams per hour, observed that with faster rates, the linolein changes to olein without appreciable change in saturated glycerides at temperatures of 154 °C. and 182 °C. As the rates decrease, the main change they observed is the disappearance of linolein and an increase in the saturated glycerides, the percentage of olein remaining constant. Their results indicate that with faster rates, the hydrogenation at these two temperatures is selective and that the selectivity disappears with slower rates. They conclude from their study that selectivity is due to the nature of the catalyst, not to the process.

Contradictory views as to the dependence of selectivity on the

nature of the catalyst are expressed by Joglekar and Jatkar[19] in a continuation of the studies by Athavale and Jatkar. They claim that the oil used by these workers was far from pure and, when using reliable samples, their results indicate that selectivity of hydrogenation is more dependent on the method and not on the catalyst. The results of this investigation indicate that at lower flow rates, and, consequently, more contact time with the hydrogen, the percentage decrease in iodine value is greater than at the higher rates. The results also indicate that during the course of the hydrogenation of unsaturated oils the nature of the reaction depends upon the relative concentrations of linolein and olein in the oil. The linolein is predominately converted into stearin when linolein and olein are in the approximate ratio of 1:1 as is characteristic of cottonseed oil regardless of the flow rates, and the hydrogenation is said to be non-selective. On the other hand, it is claimed that when the ratio is approximately equal to 1:0.25 as in safflower oil, selectivity is observed with faster rates of the flow of oil. Therefore, in general, the course of the reaction of linolein hydrogenation appears to be a function of the relative concentration of linolein and olein in the oil and the flow of the oil over the catalyst.

Patents[20] granted to Mills, Sanders and Hawley in 1950 describe a continuous process for the hydrogenation of vegetable oils. Their system consists of an oil supply tank, tubular preheater, catalyst mixing tank which supplies a suitable catalyst that is pumped directly into the pipeline, hydrogenator, hydrogen holder, compressor unit, and

heat exchange equipment. The internal dimensions of this hydrogenator were a diameter of eight inches and a height of ninety-seven inches. It was equipped with a mechanical agitator of 200 RPM, baffles, and it was capable of causing extreme turbulence. The authors claim that when the hydrogenation reaction is greatly speeded up, so that the desired end point is reached in a matter of a few minutes, by the employment of adequate amounts of catalyst, violent agitation, and superatmospheric hydrogen pressure, an unexpected degree of repression of the formation of iso-oleic glyceride occurs, the extent being so beneficial as to more than offset those aspects of the process which are unfavorable from the point of view of obtaining selectivity. This increased agitation has in the past been found by most investigators to be detrimental to selectivity, namely, to be favorable to stearic glyceride formation. They also state that the outstanding aspect of the process is the improvement in product quality which results directly or indirectly from the very high reaction rates which it employs, even when other operating variables of the process are within undesirable ranges from the standpoint of selection as contrasted with the corresponding product characteristics produced by the slower hydrogenation rates (at corresponding temperatures) which characterize prior practices. As an example of this process, they claim that with a refined cottonseed oil supplied at a rate of 1,000 pounds per hour, hydrogen inlet rate of 634 cubic feet per hour, hydrogen pressure of 50 psig, catalyst concentration of 0.044 percent nickel in the oil, and oil temperature of 167 °C., they were able to reduce the iodine value from

112.0 to 69.5 in three minutes; however, in any examples dited, they do not list the amounts of the major constituents of either the feed or product, and merely state that the products have "excellent plastic properties and good keeping qualities" and that the increase in free fatty acid resulting from partial hydrolysis during hydrogenation was about 0.01%, whereas conventional batch process product compared to it increases from about 0.03% to 0.10%. In one example in which a smaller hydrogenator was used with a flow rate of only 2.44 pounds per minute, the product was compared with the product of approximately the same iodine value from a batch process and was reported to have a smoother consistency and a lower content of iso-oleic acid esters (5.7% iso-oleic as compared with 8.6% in the batch product).

In a process patented by Sanders[21] the partial hydrogenation of unsaturated glyceride oils in an inert fat solvent is described. It is claimed that by catalytically hydrogenating a predominantly unsaturated vegetable oil, such as cottonseed oil, dissolved in an appropriate volatile solvent, such as ethanol, this process can reduce the linoleic glyceride content to a lower value than is possible by known means of hydrogenation, provided the reaction conditions employed fall within certain limits, before the hydrogenated product exceeds any desired upper limit of melting point. In conventional practice conditions that favor high selectivity (preferential conversion of linoleic to oleic before a material increase in stearic occurs) also favor formation of the solid iso-oleic glyceride which tends to offset the advantage gained by the high selectivity. On the contrary, Sanders

claims that this process results in improving selection to a greater extent than it increases the formation of iso-oleic glyceride. Typical comparison of changes in composition during batch operations with a solvent and without a solvent in which the percentage reduction of linoleic was the same will show that the increase in normal oleic, iso-oleic, and saturated stearic was 5.1, 20.6, and 15.3% respectively without a solvent and 5.4, 30.6, and 5.0 with a solvent. It is claimed that this method can be utilized on a continuous basis by employing the system described in earlier patents to Mills, Sanders and Hawley[20]. One example cited in which the continuous process was used fails to give the percentage of major constituents of the product so that comparison of the degree of selectivity and formation of iso-oleic glycerides with those of the batch process is possible.

A patent[22] granted to Potts and Morris, and assigned to Armour and Company, describes a process of continuously hydrogenating and deodorizing edible oils. This process is similar to previous processes in that the catalyst, oil, and hydrogen pass continuously through a hydrogenator in which mechanical agitation is produced. It differs in that the hydrogenated oil is deodorized continuously without exposure to air as is usual in ordinary batch processes. It is claimed that this process is selective with the resultant product being substantially uniform and homogeneous, but no data is included as to the relative increase of iso-oleic, oleic, and stearic glycerides.

EQUIPMENT AND ACCESSORIES

The equipment used in this investigation was essentially the same as that described by Ivey[27] in a M. S. thesis of June, 1951, except for some changes and additions.

The system consists of forty-seven feet of schedule 40 $1\frac{1}{2}$ inch steel pipe arranged on a specially constructed pipe rack. A cylindrical surge tank 16 inches in diameter and 10 inches high received the oil and in turn supplies oil to a positive displacement pump rated at 100 lb./in.^{2} pressure against zero head and a maximum rate of 20 gallons per minute. The system is provided with a $1\frac{1}{2}$ inch visible check valve located on the discharge side of the pump. This valve is followed by the hydrogen single nozzle jet injector with a throat of 0.015 inch through which either hydrogen or nitrogen can be admitted from gas cylinders by means of reducing valves, swing check valve, gate valves, and $\frac{1}{4}$ inch steel pipe. The system is provided with a glass thermometer inserted through a drilled $1\frac{1}{2}$ inch pipe cap into the process piping at approximately the mid-point of the hydrogenation zone. A gate valve is located at the downstream end of the process piping just prior to the surge tank to regulate the system pressure on a 0-100 psig pressure gauge immediately upstream from the valve. This brief discussion describes the path of the oil and gas during the preheat and hydrogenation periods as used by Ivey.

In order that the rate of flow can be more accurately measured, a bead-guided Stabil-Vis Fischer and Porter rotameter was installed

in the process piping immediately upstream from the pressure regulating valve. This instrument has a capacity of 7.8 gallons per minute of water and replaced the method of measuring the flow rate by a calibrated vernier by-pass on the pump as used by Ivey. Better regulation of flow rates is obtained by replacing the pressure reducing gate valve with a globe valve. Also an iron-constantan thermocouple was placed in a thermometer well at the pump discharge and connected to a Wheelco potentiometer-type temperature indicator.

Heat in the previous usage of the system was supplied by three electrical heaters, a Westinghouse Corox 2000 watt immersion heater located in the surge tank and two auxiliary nichrome wire heaters, each of 650 watts and wound around the $1\frac{1}{2}$ inch pipe To decrease the preheating time three additional resistance heaters were added to the system in this study. Two 600 watt heaters of 18 gauge Chromel-A wire were wound around horizontal sections of the process piping. A 1300 watt Calrod resistance heater was inserted between the magnesia lagging and outside wall on a horizontal section of the pipe.

The system was provided with a six-plate 10x10 inch plate and frame Sperry cast iron filter press to separate the catalyst from the hydrogenated oil. The main pump was used to develop filtration pressure delivering the oil from the $1\frac{1}{2}$ inch process pipe system to the press through a $\frac{1}{2}$ inch connecting line. It was possible to recirculate the oil from the filtrate tray of the press back into the surge tank by means of a motor driven gear pump which served also as a means of charging the system with oil to be hydrogenated. Other accessories included

a 3/4 inch line to vent unreacted hydrogen from the surge tank to the atmosphere and suitable piping and connections for purging the system with either air or steam. A $\frac{1}{2}$ inch by-pass line with necessary valves was added to the filter press so that the filter could be pre-coated with a filter-aid by circulating through the gear pump oil to which filter-aid had been added.

EXPERIMENTAL PROCEDURE

Operating Procedure

Installation of the Fischer and Porter SBABIL-VIS rotameter for the measurement of flow rates and the two Chromel-A 18 gauge electrical resistance heaters was completed in August of 1951. Since the rotameter was calibrated for water with a capacity of 0-7.8 gallons per minute, it was necessary to correct the indicated oil flow rate for the difference in the densities. Inasmuch as the density of cottonseed oil changes less than one percent over an iodine value range of 112 to 65 at a constant temperature in the vicinity of the operating temperatures according to Wakeham and Magne[25], it was felt that a constant correction factor of 1.12 obtained from a Fischer-Porter nomograph using an average density of 0.819 gm./ml. at 350 °F. would be well within experimental limits. As this type of rotameter is not sensitive to a changing viscosity, it was not necessary to correct the flow rates for this property.

The system was charged with oil to be hydrogenated by utilizing the recirculating gear pump to which a rubber hose was attached to the suction side. The drum containing oil to be processed was placed on a Fairbanks-Morse platform scales and was pumped from, through the rubber hose, until the proper weight had been removed. During the time required for charging, it was necessary to start the main pump to prevent the system from flooding. As soon as the system had been charged, the electrical heaters were turned on, and the oil circulated through

the system at the maximum flow rate with nitrogen bubbling through the oil to prevent oxidation. Since the pre-heating required over four hours, as was seen from the first few runs, it was necessary to add the 1300 watt Calrod heating unit to the system. With this additional source of heat, the time required for pre-heating was reduced approximately $3\frac{1}{2}$ hours.

When the oil had been heated to the approximate desired operating temperature, the nickel catalyst was added to the circulating oil by withdrawing enough oil from the sampling cock on the surge tank to form a slurry and then pouring the hot oil-catalyst mixture into the surge tank through an opening in the top of the tank. For the first two runs (Runs A, B) 100 grams of Super-Aid Dicalite filter-aid was added to the catalyst slurry to aid in filtering the Selectol-A Cu-Ni Catalyst. As the remaining runs offered no difficulty in filtration when the Girdler G-15 Catalyst was used, it was not necessary to add filter-aid.

When the oil had reached the desired operating temperature and the catalyst was completely dispersed throughout the oil mass, the system pressure and the flow rate were regulated by adjusting the pump by-pass and the pressure reducing globe valve at the terminal of the process piping. With the system at the desired operating conditions, the flow of nitrogen was stopped. Hydrogen at a particular pressure was admitted to the system, and the run was started. In the first few runs, the heaters remained on during the run, but it was discovered that the system temperature could be maintained approximately constant by the manual "on and off" operation of the 2000 watt immersion

heater in the surge tank.

The volume of hydrogen used during the run was measured by the decrease in volume of gas in the hydrogen cylinder as indicated by the capacity scale on the pressure gauge of the two stage gas regulator. The unreacted hydrogen, after one pass through the system, was vented to the atmosphere, no attempt being made to measure its volume; however, it was possible to calculate the amount of exhausted gas from the difference in amount of gas admitted to the system and the amount of gas that had reacted with the oil. According to Arneil[24], the quantity of hydrogen reacting is directly proportional to the change in iodine value and is theoretically equal to 0.0142 cubic feet (at 0 °C. and 1 atmosphere) per pound of oil per unit of iodine value decrease. Operational data and samples were taken until the completion of the run.

Upon completion of the run, the flow of hydrogen was stopped and nitrogen again was admitted to the system. All heating elements were cut off and the oil was allowed to circulate until the temperature dropped to approximately 200 °F. Then the flow of oil and catalyst was partially diverted to the filter press, and filtration was begun. The purpose of maintaining the oil and catalyst flow was to prevent the catalyst from settling in the system. The flow diverted to the filter was recirculated into the system until a major part of the catalyst had been separated from the oil. At this point, the collection of the filtered oil stream that was recirculated was begun with the assurance that very little catalyst would settle in the system since most of it had been separated previously. As the collection of the filtered oil

neared completion, it became impossible to maintain filtration pressure with the main pump. By proper arrangement of the valves, it was then possible to complete the filtration using the compressed air to furnish the required filtration pressure.

It was necessary to pre-coat the filter only after the canvas filter cloth had been renewed. The pre-coating was accomplished by adding at the filtrate tray 150 grams of Dicalite filter-aid to a quantity of unhydrogenated oil that was recirculated from the filtrate tray through the gear pump to the filter. For the first two runs using the Drew Selectol-A Cu-Ni Catalyst, it was impossible to completely separate the catalyst from the oil due to colloidal catalyst particles while the use of the Girdler G-15 catalyst in the remaining runs offered no difficulty in the filtration operation. Also the use of the colloidal catalyst resulted in impregnating the filter cloth with colloidal metal particles so that completion of the filtration was accomplished only with difficulty and necessitated the renewal of filter cloths after Runs A and B. The filter cloth was changed only once in the remaining runs in which the Girdler G-15 catalyst was used.

Sampling Procedure

The method of sampling as used by Ivey in the preliminary work on the continuous hydrogenation of cottonseed oil was found to be satisfactory and was adopted in this investigation except for minor differences. Samples of oil for analysis were taken every fifteen minutes except for Run A in which they were taken every ten minutes.

The sampling cock located near the bottom of the surge tank was first flushed by allowing a small amount of oil to flow out. Approximately 250 ml. of oil were then collected in a flask to which had been added equal parts of filter-aid and Santocel, agitated well, and poured into a Buchner funnel equipped with a suction flask connected to an air aspirator. After a portion of the oil had passed through and a cake formed, a test tube was inserted into the flask to collect the sample.

Analytical Procedure

In order that information on the hydrogenation rate and the selectivity of the reaction could be obtained, the iodine value of all samples was determined together with the thiocyanogen value and Wiley melting point of the original oil and the final product sample. It was possible to calculate the percentages of stearic, oleic, and linoleic glycerides in the fat by the use of the iodine value in conjunction with the thiocyanogen value thereby obtaining information as to the degree of selectivity. As the iodine value is a measure of the unsaturation, these values themselves provide a measure of the hydrogenation rate, while the Wiley melting points give some indication of the higher melting materials formed by the reaction, namely the isooleic and stearic glycerides which are solid at the room temperature.

The analytical work performed in obtaining the iodine values, thiocyanogen values, and Wiley melting points was in accordance with the official methods of the American Oil Chemists Society[26].

RESULTS

The first two runs were exploratory runs since it was necessary to become familiar with the response of the system under various operating conditions. Also several unsuccessful attempts were made to separate the Drew catalyst from the oil in these two runs. Run A (see Table I) was performed with the system charged with 75 pounds of non-winterized cottonseed oil, 200 grams of Drew Selectol- A Cu-Ni catalyst containing 28 percent active metal catalyst (0.16 % nickel in the total oil mass), and 100 grams of filter-aid. In 70 minutes of hydrogenation the iodine value was reduced from 102.5 to 92.2 Run B (see Table II) was performed with the same quantity of the Drew catalyst, oil, and filter-aid. The hydrogenation reaction in this run produced a 35.6 percent increase in the saturated glycerides (see Table XV) while the iodine value was reduced from 110.5 to 79.0 in 105 minutes. The average hydrogenation rates from Runs A and B as shown by the decrease in iodine value were 0.142 iodine value units per minute and 0.300 iodine value units per minute, respectively.

Run C (see Table III) was performed with 75 pounds of non-winterized cottonseed oil and 200 grams of Girdler G-15 hydrogenation catalyst containing 20 percent active metal catalyst (0.11 % nickel in the total oil mass). As no difficulty was encountered in the final filtration of the Girdler catalyst, it was not necessary to add filter-aid in this or subsequent runs. The iodine value was reduced from 110.5 to 100.0 in 120 minutes for an average of 0.088 iodine value units per minute. The

saturated glyceride content (see Table XV) increased only 4.2 percent while the linoleic showed a reduction of 49.0 percent.

In Run D (see Table IV) 75 pounds of non-winterized cottonseed oil and 200 grams of the Girdler catalyst were used. The iodine value decreased from 112.5 to 93.0 in 90 minutes for an average rate of 0.216 iodine value units per minute. The saturated content increased to 29.6 percent and the linoleic content decreased to 35.5 percent in the final product (see Table XV).

Run E (see Table V) was performed with 75 pounds of the non-winterized cottonseed oil and 200 grams of the Girdler catalyst. The iodine value was reduced from 112.0 to 89.2 in 120 minutes for an average hydrogenation rate of 0.190 iodine value units per minute. The saturated glyceride content (see Table XV) increased to 28.3 percent, and the linoleic content was reduced to 27.1 percent in the final product.

Run F (see Table VI) was performed with the same quantity of oil and Girdler catalyst as Run E. The degree of unsaturation decreased from an iodine value of 112.5 to 77.2 in 120 minutes for an average rate of 0.294 iodine value units per minute. The saturated glyceride content (see Table XV) increased to 28.9 percent while the linoleic decreased to 14.9 percent in the final product.

Run G (see Table VII) performed with the same charge of oil and Girdler catalyst as Run E. The 111.5 iodine value of the original was reduced to 80.5 in 90 minutes for an average rate of 0.345 iodine value units per minute. The saturated glycerides (see Table XV) increased to 27.4 percent, and the linoleic was reduced to 16.5 percent.

Run H (see Table VIII) was performed with 75 pounds of non-winterized cottonseed oil and 200 grams of the Girdler catalyst. An average hydrogenation rate of 0.326 iodine value units per minute was obtained in decreasing the iodine value from 111.6 to 72.4 in 120 minutes. The saturated glycerides (see Table XV) increased only slightly to 25.9 percent while the linoleic content was reduced to 6.4 percent.

Run I (see Table IX) was performed with 75 pounds of non-winterized cottonseed oil and 200 grams of the Girdler catalyst. The iodine value was reduced from 109.4 to 91.3 in 120 minutes for an average rate of 0.151 iodine value units per minute. The saturated content (see Table XV) increased to 25.2 percent while the linoleic decreased to 26.0 percent.

Run J (see Table X) was performed with 75 pounds of winterized cottonseed oil and 200 grams of the Girdler catalyst. The degree of unsaturation was reduced from an iodine value of 112.0 to 97.5 in 105 minutes for an average rate of 0.138 iodine value units per minute. The saturated glycerides (see Table XV) increased to 20.7 percent, and the linoleic glycerides decreased to 28.2 percent.

In Run K (see Table XI) the charge to the system was the same as in Run J. This run reduced the iodine value from 112.3 to 77.2 in 120 minutes for an average rate of 0.292 iodine value units per minute. The saturated glycerides (see Table XV) increased to 23.4 percent while the linoleic content was reduced to 9.2 percent.

For Run L (see Table XII) the amount of Girdler catalyst used was increased to 300 grams which corresponds to a 0.17 percent nickel in the total mass of 75 pounds of winterized cottonseed oil. In 120 minutes

the iodine value was reduced from 112.5 to 85.3 for an average rate of 0.226 iodine value units per minute. The saturated glycerides (see Table XV) increased to 21.3 percent, and the linoleic content was decreased to 15.8 percent in the final product.

Run M (see Table XIII) was performed with the same charge as used in Run L. The average hydrogenation rate of 0.256 iodine value units per minute reduced the iodine value of the original oil from 112.5 to 81.8 in 120 minutes. The saturated glyceride content (see Table XV) was increased to 21.4 percent while the linoleic content was reduced to 12.4 percent.

Run N (see Table XIV) was performed with the same charge as used in Run L. The iodine value was reduced from 112.5 to 69.5 in 120 minutes for an average reaction rate of 0.358 iodine value units per minute. The linoleic glyceride content (see Table XV) was nearly eliminated while the saturated glycerides increased to 21.4 percent.

DISCUSSION OF RESULTS

Effect of Rate of Flow

The effect of flow rates over a limited range on the rate of hydrogenation under the various conditions of the different runs may be seen from Figures 1-4. As shown in Figure 1, there is a decrease of 14.1 percent in the iodine value in Run I as compared with a decrease of 13.0 percent in Run J over a period of 105 minutes, flow rates being 8.4 and 6.2 GPM, respectively, with other conditions in the system being identical. In other words, the average rate of hydrogenation, 0.151 and 0.138 iodine value units per minute, respectively, increased with the increased flow rate of Run I. Figure 2 shows the effect of flow rates on the hydrogenation rate and differs from Figure 1 in that the hydrogen pressure of Runs C, D, E, and F was 20 psig instead of 15 psig as in Runs I and J. Under the conditions of these runs, the average hydrogenation rates were 0.088 (4.2 GPM), 0.190 (6.2 GPM), 0.216 (8.4 GPM), and 0.294 (8.8 GPM) iodine value units per minute for Runs C, E, D, and F, respectively, and too, increased with the increased flow rates. For various undetermined reasons, contradictory results were obtained for Runs K and H (see Figure 3) in that the average hydrogenation rate for Run K (8.4 GPM) was 0.292 iodine value units per minute as compared to that of 0.326 iodine value units per minute for Run H (6.2 GPM). Conditions for Runs K and H differed from those of the runs shown in Figures 1 and 2 in that the hydrogen pressure was increased further to 25 psig, other conditions being identical. Also, a decrease in the average hydrogenation rate of 0.256

to 0.226 iodine value units per minute for Runs M and L, was observed (see Figure 4) for the increased flow rate of Run L (8.4 GPM) as compared to Run M (6.2 GPM). These two runs differed from those shown in Figure 2 in that 300 grams of catalyst were used. On the basis of the runs shown in Figures 1-4, the hydrogenation rate appears to increase with an increased flow rate under some conditions while, under other conditions, it decreases. On the basis of Run H which produced the best results in terms of selectivity and reaction rate, the length of continuous $1\frac{1}{2}$ inch pipe necessary to obtain similar results as those obtained in this work would be 8070 feet.

Effect of Hydrogen Pressure

The effect of hydrogen pressure on the hydrogenation rate is shown in Figures 5 and 6. The average rates for Run J (hydrogen pressure of 15 psig) (see Figure 5) are 0.138 iodine value units per minute, for Run E (hydrogen pressure of 20 psig), 0.190 iodine value units per minute, and for Run H (hydrogen pressure of 25 psig), 0.326 iodine value units per minute. This increase of hydrogenation rate with increased hydrogen pressure is also exhibited by Runs I, D, and K (see Figure 6). The average rates are 0.151, 0.216, and 0.292 iodine value units per minute for hydrogen pressures of 15, 20, and 25 psig. These runs differ from those in Figure 5 in that the flow rate is 8.4 GPM instead of 6.2 GPM. Under the conditions of the runs in the study, an increased hydrogen pressure caused an increase in the hydrogenation rate. The amount of hydrogen exhausted to the atmosphere is dependent, other operating variables constant, on the hydrogen pressure, and, therefore the amount

admitted to the system. For example, the greatest average reaction rate was obtained in Run N (0.358 iodine value units per minute) in which the hydrogen pressure was 25 psig. Of a total of 62 cubic feet of hydrogen admitted to the system, 46 cubic feet reacted with the oil, and 16 cubic feet were vented to the atmosphere. In other words, the average hydrogen entrance rate was 0.51 cubic feet per minute, the average rate at which the hydrogen was absorbed was 0.38 cubic feet per minute, and the exit rate was 0.13 cubic feet per minute. The hydrogen efficiency was 74 percent. By comparison, in Run L all operating conditions were identical to Run N except the hydrogen pressure which was 20 psig. The average hydrogenation rate of 0.226 iodine value units per minute was noticeably lower. Of a total of 49 cubic feet of hydrogen admitted, 29 cubic feet reacted with the oil for a hydrogen efficiency of 59 percent. On the basis of this comparison, it seems that the greater reaction rate of Run N is due to the increased agitation produced by the higher hydrogen pressure, possibly to the larger amount of excess hysrogen present in the first part of the process piping, but the reaction rate does not appear to be dependent to any great extent on the excess hydrogen present as indicated by the smaller reaction rate and the larger amount of hydrogen exhausted in Run L.

Effect of Catalyst Concentration

From the study of Figures 7-9 it can be seen that the average rates of hydrogenation increased with an increased concentration of catalyst although the difference is not as pronounced in Figure 8 as it is in Figures 7 and 9.

Effect of Temperature

The effect of temperature (see Figure 10) on the rate of hydrogenation is as expected. In Run K the temperature ranged from 350 to 354 °F., and the average rate of hydrogenation was 0.292 iodine value units per minute. In Run G the temperature range was 380 to 398 °F., and the average rate of hydrogenation was 0.345 iodine value units per minute. From the results of these two runs, it can be seen that the hydrogenation rate increased with the higher temperature.

Selectivity

Since most of the all-hydrogenated shortenings made from cottonseed oil have a linoleic content of 5 to 12 percent, a saturated content of 27 to 33 percent, and a Wiley melting point of 95-98 °F., it can be seen from Table XV that the product of Runs F, H, K, and N meets entirely of approximately these specifications. In terms of relative selectivity, the reaction of Run H had a greater degree of selectivity (see Table XV) than the other runs as the linoleic content was almost eliminated while the saturated content increased to an extent less than the remaining runs.

CONCLUSIONS

1. This investigation indicates that it is possible to obtain a product from a continuous process that is similar to an all-hydrogenated product obtained from a batch process.

2. Selective catalytic hydrogenation of cottonseed oil is possible in a continuous process as was observed by the large decrease of linoleic glycerides without a material increase in the saturated content. The degree of selectivity appears to depend, among other things, on the rate of flow, method of the hydrogenation process itself, and the relative amounts of linoleic and oleic glycerides present in the original oil.

3. The hydrogenation rate does not necessarily increase with an increased flow rate. The remaining conditions under which the hydrogenation is performed tends to influence the effect of flow rate on the reaction rate.

4. The hydrogenation rate increases with an increase in the catalyst concentration. The effect is more pronounced in some cases.

5. The hydrogenation rate increases with greater hydrogen pressure and higher temperatures in all cases within the limits of this investigation as was expected.

6. On the basis of this investigation, it is not difficult to picture a continuous hydrogenating system consisting of a series of hydrogen jets at intervals of 47 feet in the process piping in which the flowing oil is reduced in unsaturation to an extent dependent upon the total length of pipe in the system.

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APPENDIX I

TABLE I

RUN A*

75 Lbs. of Non-winterized Cottonseed Oil (Buckeye)

Time (Min)	T. (°F)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	330	10	20	168	5.3	A1	102.5
10	334	11	20	163	5.3	A2	100.2
20	337	10	20	160	5.4	A3	98.8
30	340	10	20	157	5.3	A4	98.0
40	342	12	20	153	5.2	A5	96.4
50	345	10	20	149	5.3	A6	95.0
60	347	10	20	145	5.4	A7	93.5
70	348	10	20	142	5.3	A8	92.2

* 200 grams Selectol-A Cu-Ni Catalyst (Drew).
100 grams Super-Aid Dicalite filter aid added with the catalyst.
System Pressure: 10 psig.
26 Ft^3 of hydrogen at 70 °F. and 1 atmosphere.
Average flow rate at 350 °F. during run: 5.3 GPM.

TABLE II

RUN B*

75 Lbs. of Non-winterized Cottonseed Oil (Buckeye)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	325	16	30	142	8.1	B1	110.5
10	330	16	30	137	8.0	--	
15	-	-	-	-	-	B2	
20	334	15	30	130	8.2	--	
30	337	16	30	123	8.1	B3	
40	343	17	30	115	8.0	--	
50	346	17	30	110	8.0	B4	
60	349	18	30	103	7.9	B5	
70	352	17	30	97	8.0	--	
75	-	-	-	-	-	B6	
80	354	18	30	92	7.9	--	
90	356	20	30	85	8.2	B7	
100	357	17	30	80	7.9	--	
105	357	17	30	78	7.9	B8	79.0

* 200 grams Selectol-A Cu-Ni Catalyst (Drew).
150 grams Super-Aid Dicalite filter-aid used to precoat the filter press.
64 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during the run: 8.0 GPM.
System pressure: 17 psig.

TABLE III

RUN C*

75 Lbs. of Non-winterized Cottonseed Oil (Buckeye)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	315	10	20	75	3.8	C1	110.5
10	317	10	20	73	3.9		
15	-	-	-	-	-	C2	-
20	320	10	20	72	3.9		
30	322	10	20	71	3.9	C3	-
40	325	10	20	68	3.9		
45	-	-	-	-	-	C4	-
50	327	10	23	62	4.1		
60	330	10	22	59	4.4	C5	-
70	334	10	21	55	4.6		
75	-	-	-	-	-	C6	106.3
80	337	10	22	48	4.5		
90	339	10	21	44	4.7	C7	104.6
100	342	10	21	40	4.5		
105	-	-	-	-	-	C8	101.5
110	345	10	21	30	4.4		
120	349	10	20	24	4.3	C9	100.0

* 200 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler).
51 Ft^3 of hydrogen at 70 °F. and 1 atmostphere pressure.
Average flow rate at 350 °F. during run: 4.2 GPM.
System pressure: 10 psig.

TABLE IV

RUN D*

75 Lbs. of Non-winterized Cottonseed Oil (Swift)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	325	10	20	223	8.5	D1	112.5
10	329	10	20	218	8.5		
15	-	-	-	-	-	D2	111.0
20	333	10	20	214	8.5		
30	336	10	20	209	8.4	D3	108.7
40	341	10	20	204	8.5		
45	-	-	-	-	-	D4	105.5
50	346	10	20	200	8.5		
60	349	10	20	195	8.4	D5	102.0
70	352	10	20	190	8.5		
75	-	-	-	-	-	D6	97.4
80	354	10	20	184	8.3		
90	356	10	20	180	8.3	D7	93.0

* 200 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
43 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during run: 8.4 GPM.
System pressure: 10 psig.

TABLE V

RUN E*

75 Lbs. of Non-winterized Cottonseed Oil (Swift)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	354	10	20	177	6.2	E1	112.0
10	355	10	20	173	6.2		
15	-	-	-	-	-	E2	-
20	357	10	20	170	6.2		
30	359	10	20	165	6.1	E3	108.0
40	361	10	20	160	6.3		
45	-	-	-	-	-	E4	103.8
50	363	10	20	155	6.1		
60	365	10	20	150	6.1	E5	102.5
70	366	10	20	145	6.2		
75	-	-	-	-	-	E6	98.0
80	367	10	20	140	6.3		
90	365	10	20	136	6.1	E7	95.6
100	366	10	20	130	6.4		
105	-	-	-	-	-	E8	92.7
110	366	10	20	125	6.3		
120	365	10	20	121	6.2	E9	89.2

* 200 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
56 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during run: 6.2 GPM.
System pressure: 10 psig.

TABLE VI

RUN F*

75 Lbs. of Non-winterized Cottonseed Oil (Swift)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	336	10	20	121	8.4	F1	112.5
10	340	10	20	116	8.5		
15	-	-	-	-	-	F2	108.5
20	345	10	20	112	8.7		
30	348	10	20	107	9.0	F3	105.5
40	355	10	20	102	8.6		
45	-	-	-	-	-	F4	101.5
50	358	10	20	98	9.0		
60	362	10	20	95	9.0	F5	97.2
70	364	10	20	90	9.0		
75	-	-	-	-	-	F6	92.5
80	366	10	20	85	8.9		
90	367	10	20	80	9.0	F7	86.5
100	365	10	20	75	9.0		
105	-	-	-	-	-	F8	82.0
110	366	10	20	72	8.9		
120	365	10	20	68	9.0	F9	77.2

* 200 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
53 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during run: 8.8 GPM.
System pressure: 10 psig.

TABLE VII

RUN G*

75 Lbs. of Non-winterized Cottonseed Oil (Swift)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	380	10	25	8.5	65	G1	111.5
10	382	10	25	8.1	60		
15	-	-	-	-	-	G2	106.2
20	395	10	25	8.2	53		
30	396	10	25	8.2	45	G3	102.8
40	398	10	25	8.4	40		
45	-	-	-	-	-	G4	97.0
50	395	10	25	8.4	34		
60	393	10	25	8.2	23	G5	91.1
70	391	10	25	8.4	15		
75	-	-	-	-	-	G6	87.1
80	388	10	25	8.3	9		
90	387	10	25	8.4	0	G7	80.5

* 200 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
65 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during run: 8.4 GPM.
System pressure: 10 psig.

TABLE VIII

RUN H*

75 Lbs. of Non-winterized Cottonseed Oil (Buckeye)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	350	10	25	220	6.2	H1	111.6
10	349	10	25	213	6.4		
15	-	-	-	-	-	H2	108.3
20	352	10	25	206	6.0		
30	351	10	25	200	6.1	H3	102.3
40	349	10	25	194	6.3		
45	-	-	-	-	-	H4	97.0
50	352	10	25	186	6.4		
60	352	10	25	180	6.1	H5	90.6
70	350	10	25	174	6.2		
75	-	-	-	-	-	H6	85.1
80	353	10	25	168	6.3		
90	355	10	25	162	6.0	H7	80.6
100	355	10	25	157	6.3		
105	-	-	-	-	-	H8	76.4
110	352	10	25	150	6.0		
120	351	10	25	144	6.1	H9	72.4

* 200 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
76 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. and during run: 6.2 GPM.
System pressure: 10 psig.

TABLE IX

RUN I*

75 Lbs. of Non-winterized Cottonseed Oil (Buckeye)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	350	10	15	143	8.4	I1	109.4
10	350	10	15	140	8.3		
15	-	-	-	-	-	I2	107.8
20	351	10	15	138	8.3		
30	353	10	15	136	8.4	I3	106.3
40	354	10	15	133	8.5		
45	-	-	-	-	-	I4	104.1
50	352	10	15	131	8.3		
60	353	10	15	129	8.3	I5	101.3
70	354	10	15	127	8.5		
75	-	-	-	-	-	I6	99.5
80	355	10	15	125	8.4		
90	355	10	15	122	8.5	I7	96.7
100	354	10	15	120	8.4		
105	-	-	-	-	-	I8	94.1
110	355	10	15	117	8.2		
120	355	10	15	115	8.4	I9	91.3

* 200 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
28 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during run: 8.4 GPM.
System pressure: 10 psig.

TABLE X

RUN J*

75 Lbs. of Winterized Cottonseed Oil (Swift)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	353	10	15	115	6.2	J1	112.0
10	353	10	15	113	6.1		
15	-	-	-	-	-	J2	110.5
20	352	10	15	110	6.1		
30	353	10	15	108	6.1	J3	109.0
40	351	10	15	105	6.2		
45	-	-	-	-	-	J4	105.3
50	350	10	15	103	6.3		
60	350	10	15	101	6.2	J5	103.8
70	351	10	15	99	6.2		
75	-	-	-	-	-	J6	102.2
80	352	10	15	96	6.2		
90	353	10	15	93	6.2	J7	99.7
100	354	10	15	90	6.2		
105	353	10	15	89	6.2	J8	97.5

* 200 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
26 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during run: 6.2 GPM.
System pressure: 10 psig.

TABLE XI

RUN K*

75 Lbs. of Winterized Cottonseed Oil (Swift)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	350	10	25	89	8.4	K1	112.3
10	352	10	25	82	8.4		
15	-	-	-	-	-	K2	109.5
20	352	10	25	76	8.4		
30	353	10	25	70	8.5	K3	105.2
40	351	10	25	64	8.3		
45	-	-	-	-	-	K4	100.2
50	353	10	25	58	8.4		
60	353	10	25	51	8.3	K5	94.2
70	351	10	25	45	8.5		
75	-	-	-	-	-	K6	90.8
80	354	10	25	39	8.4		
90	354	10	25	32	8.5	K7	85.3
100	352	10	25	24	8.4		
105	-	-	-	-	-	K8	81.2
110	350	10	25	16	8.3		
120	353	10	25	8	8.4	K9	77.2

* 200 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler) 81 Ft^3 at 70 °F. and 1 atmosphere pressure of hydrogen.
Average flow rate at 350 °F. during run: 8.4 GPM.
System pressure: 10 psig.

TABLE XII

RUN L*

75 Lbs. of Winterized Cottonseed Oil (Swift)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	350	10	20	233	8.4	L1	112.5
10	354	10	20	230	8.3		
15	-	-	-	-	-	L2	111.2
20	353	10	20	225	8.1		
30	352	10	20	220	8.4	L3	108.0
40	350	10	20	217	8.6		
45	-	-	-	-	-	L4	104.8
50	354	10	20	212	8.5		
60	353	10	20	207	8.5	L5	100.3
70	352	10	20	202	8.4		
75	-	-	-	-	-	L6	96.6
80	353	10	20	198	8.4		
90	352	10	20	193	8.4	L7	92.5
100	352	10	20	189	8.3		
105	-	-	-	-	-	L8	89.8
110	353	10	20	184	8.4		
120	352	10	20	180	8.4	L9	85.3

* 300 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
53 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during run: 8.4 GPM.
System pressure: 10 psig.

TABLE XIII

RUN M*

75 Lbs. of Winterized Cottonseed Oil (Swift)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	350	10	20	180	6.2	M1	112.5
10	350	10	20	175	6.1		
15	-	-	-	-	-	M2	108.3
20	350	10	20	170	6.1		
30	351	10	20	165	6.0	M3	105.1
40	352	10	20	160	6.2		
45	-	-	-	-	-	M4	101.3
50	353	10	20	155	6.3		
60	354	10	20	151	6.2	M5	96.1
70	352	10	20	145	6.2		
75	-	-	-	-	-	M6	92.8
80	352	10	20	140	6.3		
90	352	10	20	136	6.3	M7	89.1
100	352	10	20	132	6.2		
105	-	-	-	-	-	M8	86.0
110	351	10	20	127	6.1		
120	350	10	20	122	6.2	M9	81.8

* 300 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
58 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during the run: 6.2 GPM.
System pressure: 10 psig.

TABLE XIV

RUN N*

75 Lbs. of Winterized Cottonseed Oil (Swift)

Time (Min)	T. (°F.)	P. (PSIG)	P. H_2 (PSIG)	H_2 Vol. (Ft^3)	Flow Rate (GPM)	Sample No.	Iodine Value
0	350	10	25	120	8.4	N1	112.5
10	351	10	25	113	8.3		
15	-	-	-	-	-	N2	106.2
20	352	10	25	110	8.5		
30	352	10	25	104	8.5	N3	100.7
40	352	10	25	98	8.4		
45	-	-	-	-	-	N4	96.7
50	351	10	25	92	8.5		
60	351	10	25	86	8.5	N5	90.6
70	352	10	25	81	8.4		
75	-	-	-	-	-	N6	85.2
80	353	10	25	75	8.3		
90	354	10	25	70	8.2	N7	79.5
100	353	10	25	65	8.3		
105	-	-	-	-	-	N8	74.0
110	351	10	25	60	8.6		
120	351	10	25	53	8.4	N9	69.5

* 300 grams G-15 reduced nickel-kieselguhr Hydrogenation Catalyst (Girdler)
67 Ft^3 of hydrogen at 70 °F. and 1 atmosphere pressure.
Average flow rate at 350 °F. during run: 8.4 GPM.
System pressure: 10 psig.

TABLE XV

Composition of Original and Final Cottonseed Oil

Samples from Various Runs

Sample	Wiley Melting Point, °F.	Iodine Value	T. V.*	Composition		
				Saturated	Oleic	Linoleic
Original	Liquid	102.5	-	-	-	-
Run A	-	92.2	-	-	-	-
Original	Liquid	110.5	73.4	21.5	34.7	43.8
Run B	94	79.0	63.5	30.4	51.6	18.0
Run C	90	100.0	71.5	22.4	44.2	33.4
Original	Liquid	112.5	72.2	22.8	29.5	47.7
Run D	84	93.0	62.8	29.6	34.9	35.5
Run E	88	89.2	66.0	28.3	44.6	27.1
Run F	98	77.2	64.5	28.9	56.2	14.9
Run G	96	80.5	66.2	27.4	56.1	16.5
Original	Liquid	111.6	70.0	25.6	25.3	49.1
Run H	94	72.4	66.6	25.8	67.8	6.4
Original	Liquid	109.4	71.6	23.5	31.7	44.8
Run I	93	91.3	69.0	25.2	48.8	26.0
Original	Liquid	112.0	77.4	6.6	42.5	50.9
Run J	81	97.5	73.2	20.7	51.1	28.2
Run K	95	77.2	69.1	23.4	67.4	9.2
Run L	91	85.3	71.5	21.3	62.9	15.8
Run M	90	81.8	71.0	21.4	66.2	12.4
Run N	99	69.5	68.5	21.4	78.1	0.5

* Thiocyanogen Value

APPENDIX II

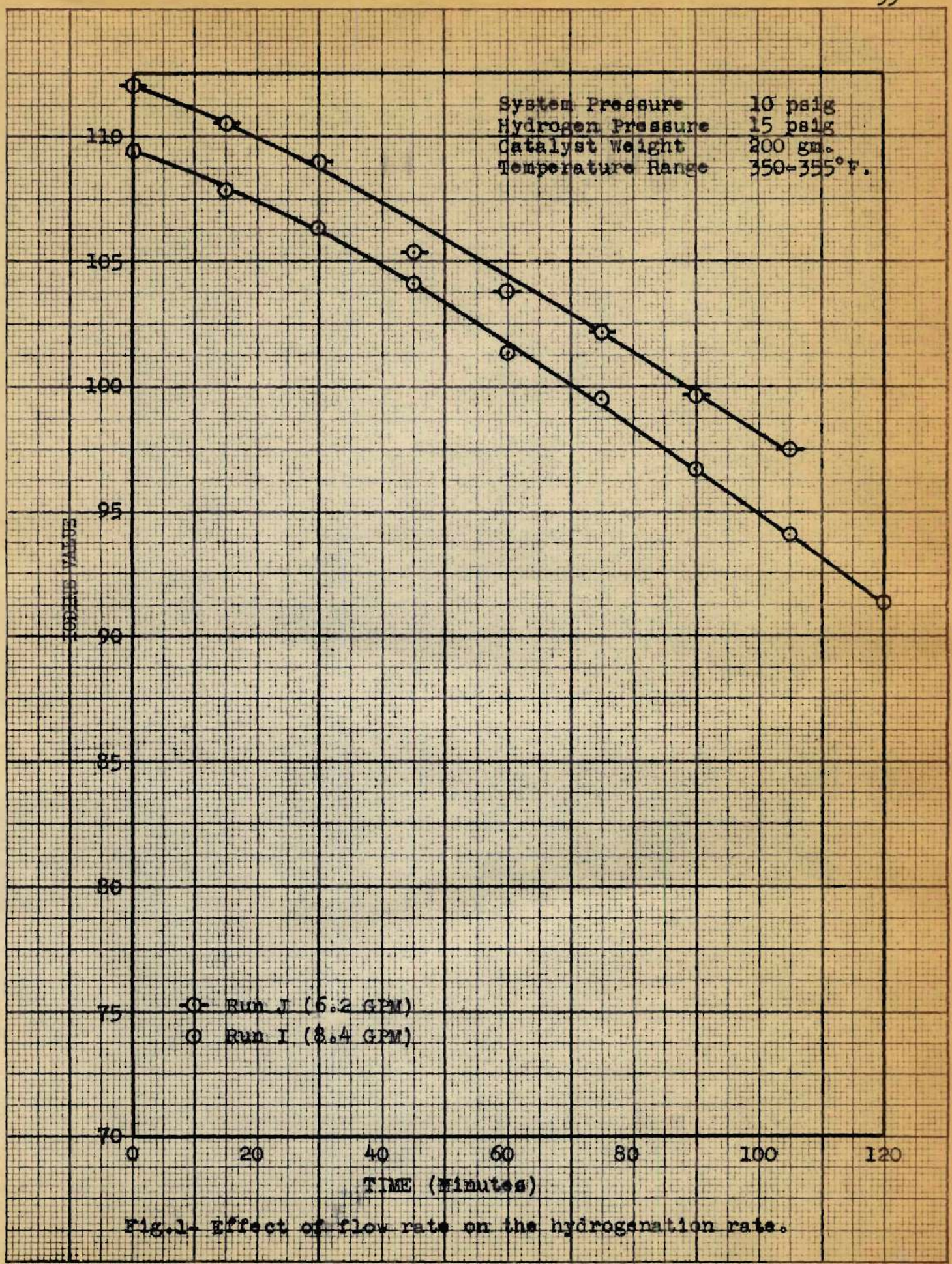


Fig.1- Effect of flow rate on the hydrogenation rate.

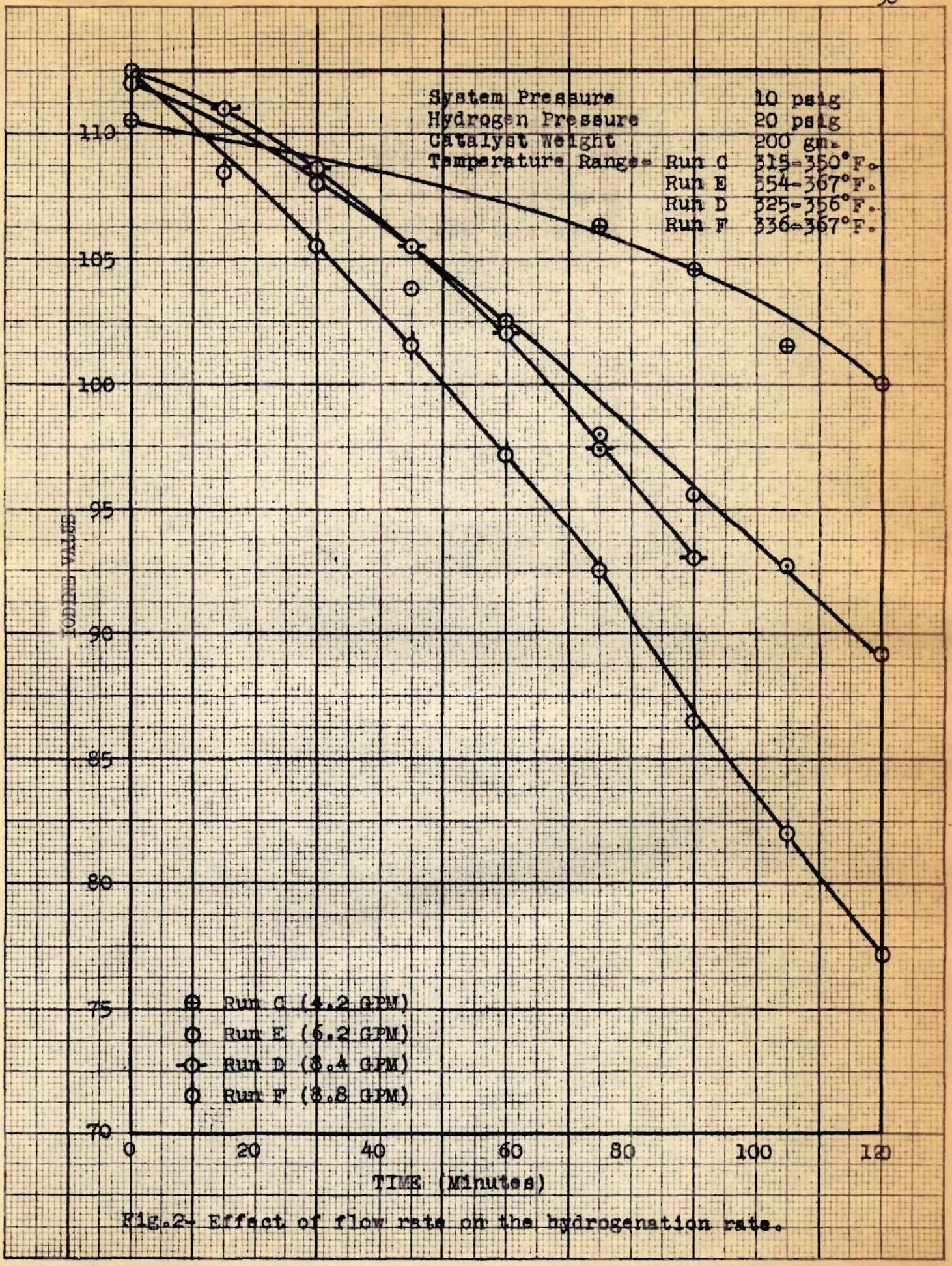


Fig. 2- Effect of flow rate on the hydrogenation rate.

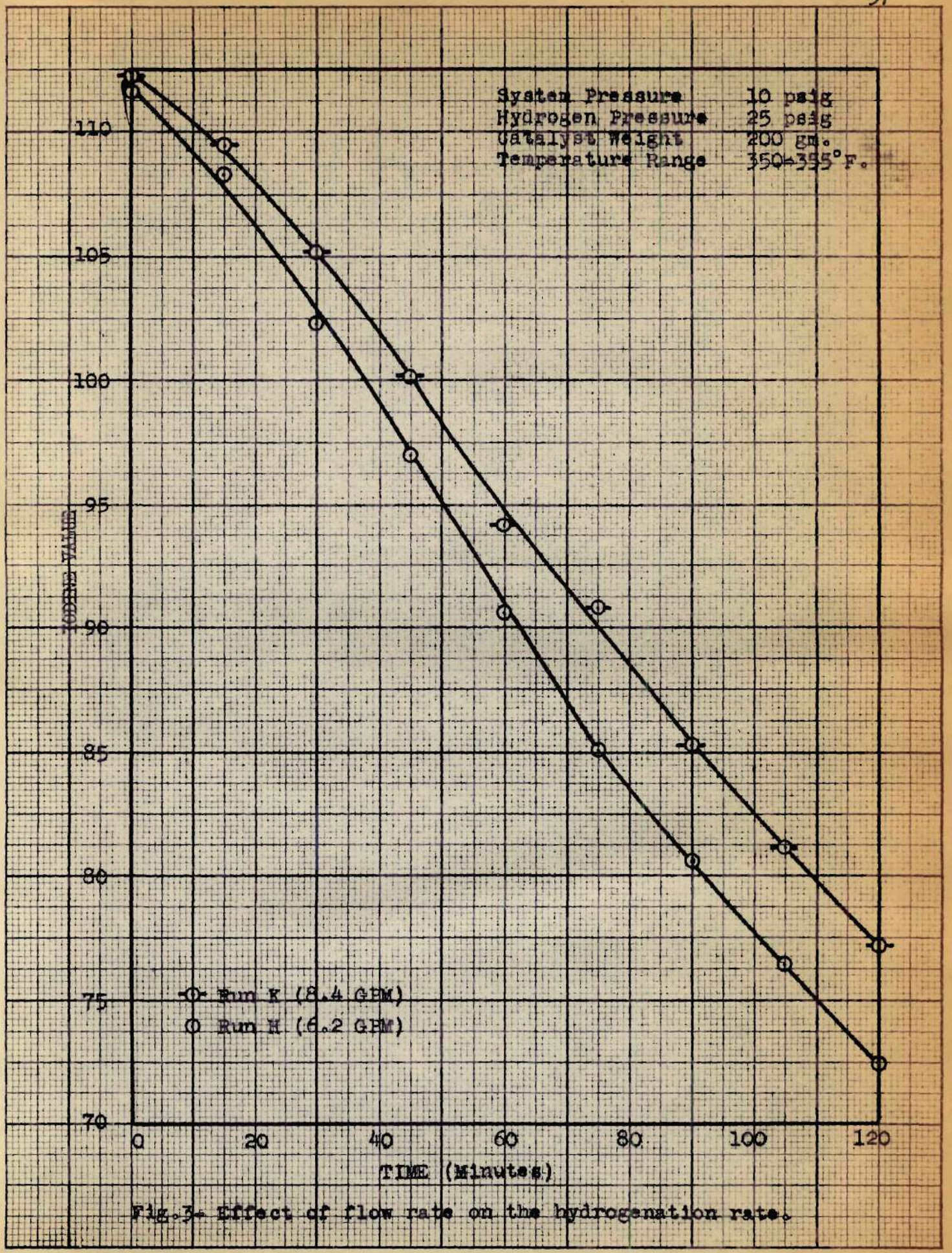


Fig. 3- Effect of flow rate on the hydrogenation rate.

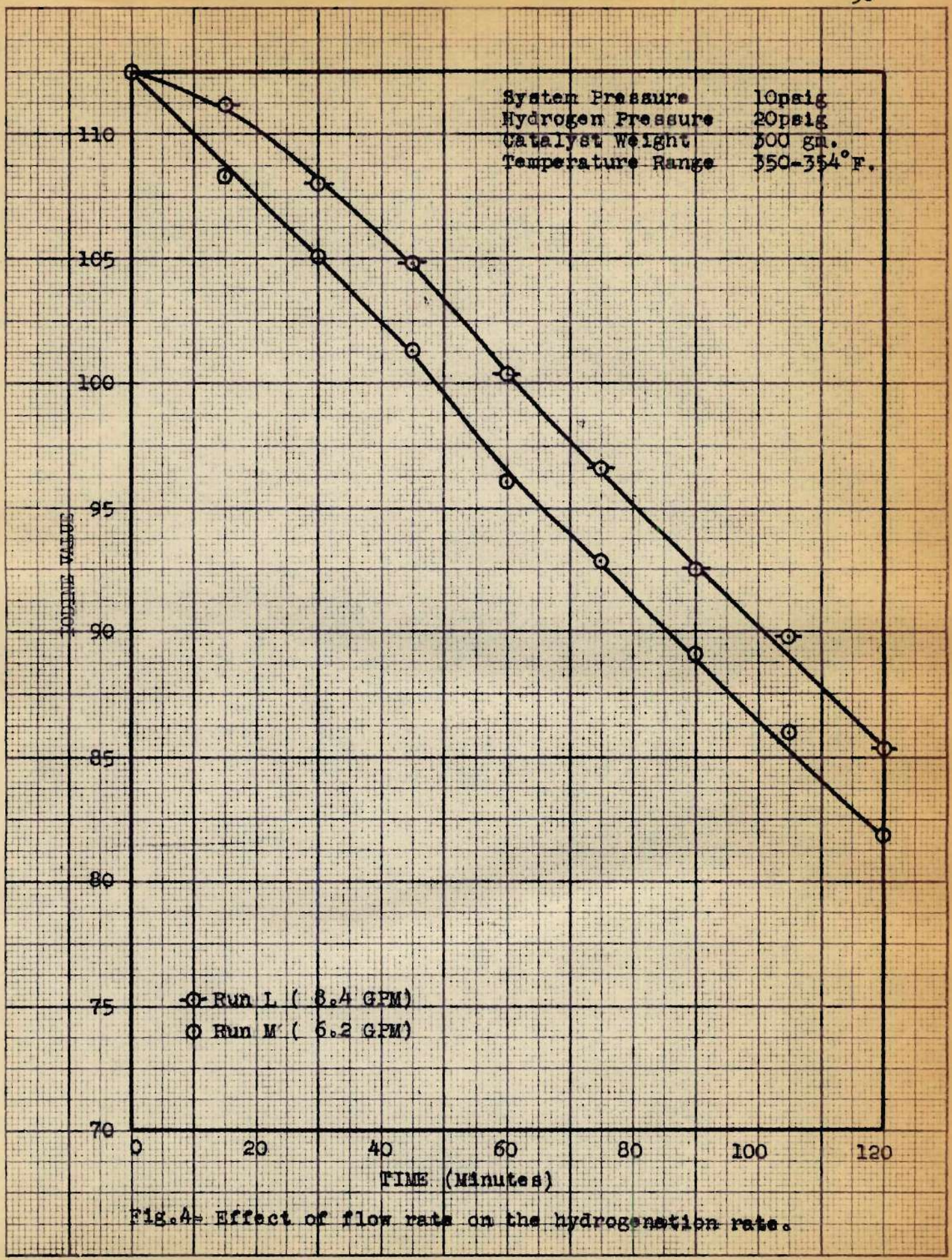


Fig.4- Effect of flow rate on the hydrogenation rate.

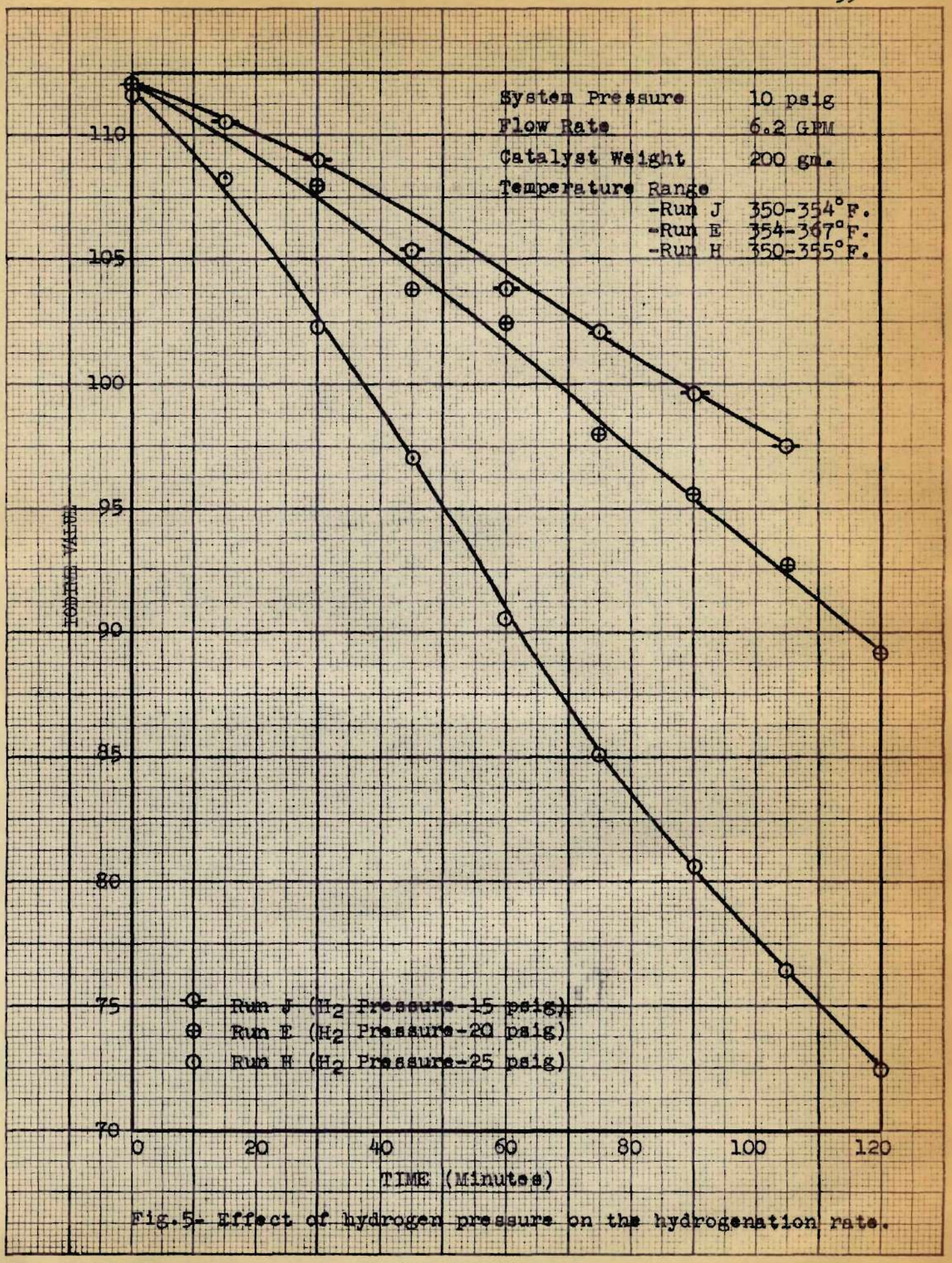


Fig.5- Effect of hydrogen pressure on the hydrogenation rate.

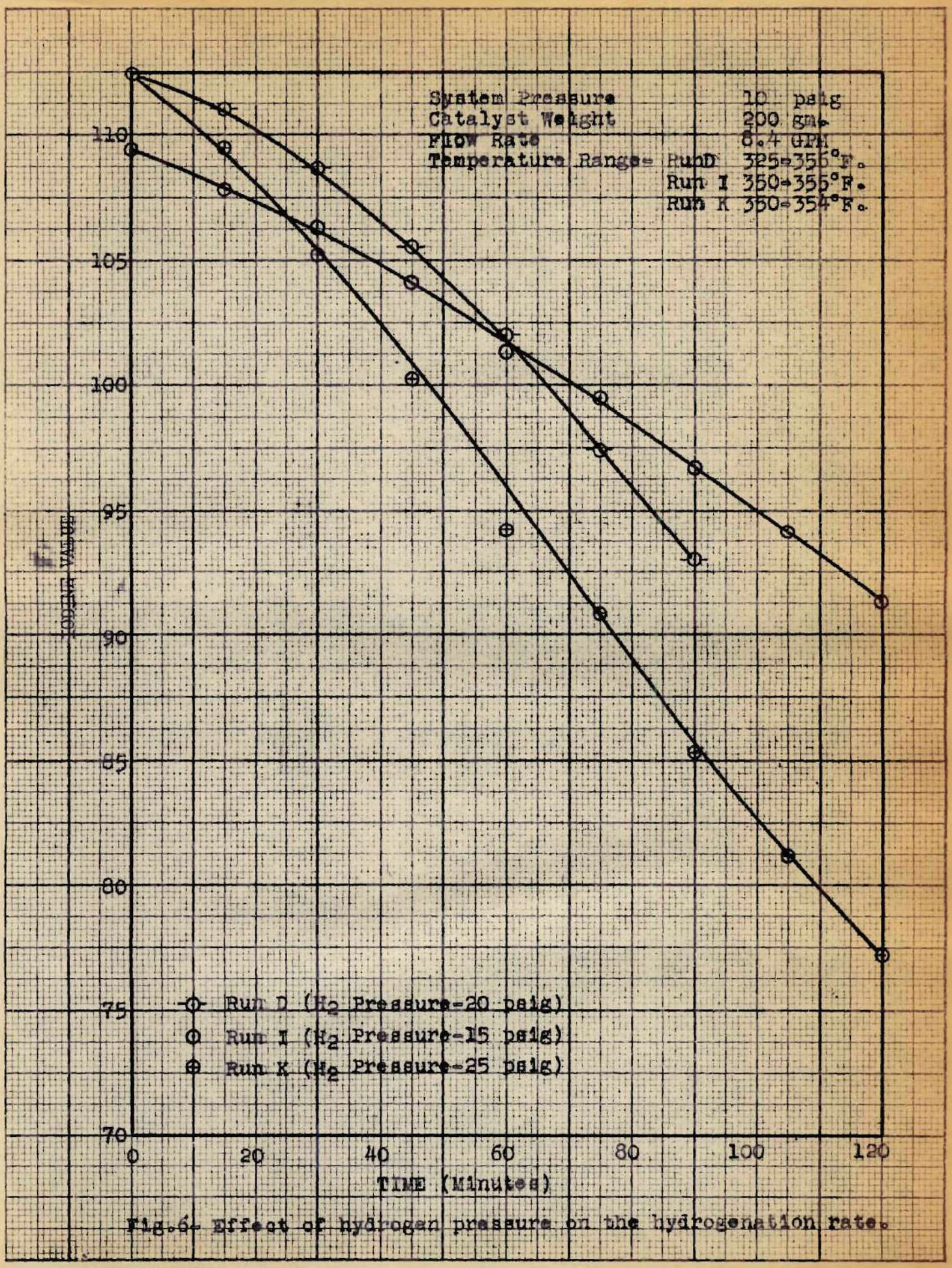


Fig.6- Effect of hydrogen pressure on the hydrogenation rate.

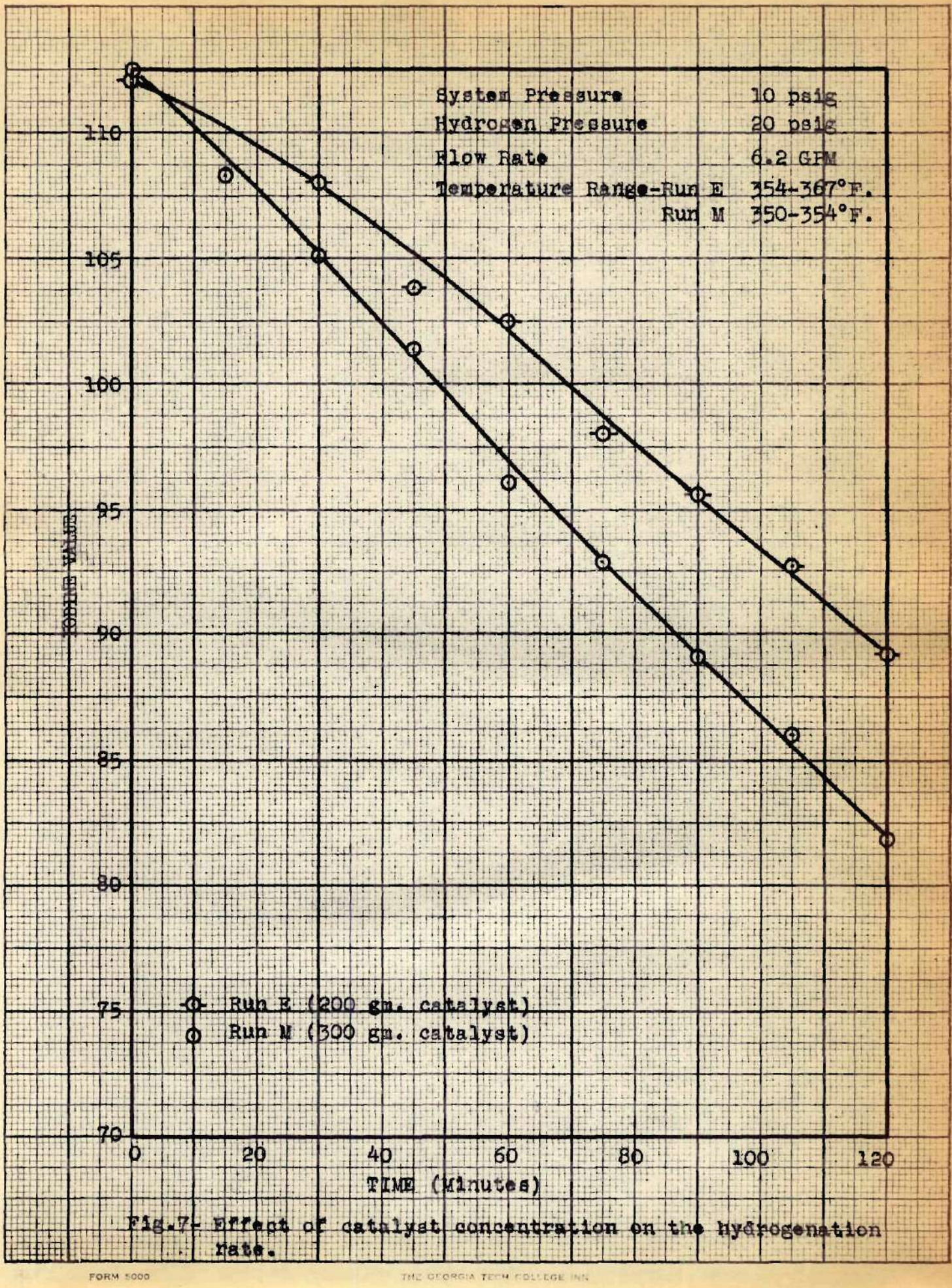


Fig.7- Effect of catalyst concentration on the hydrogenation rate.

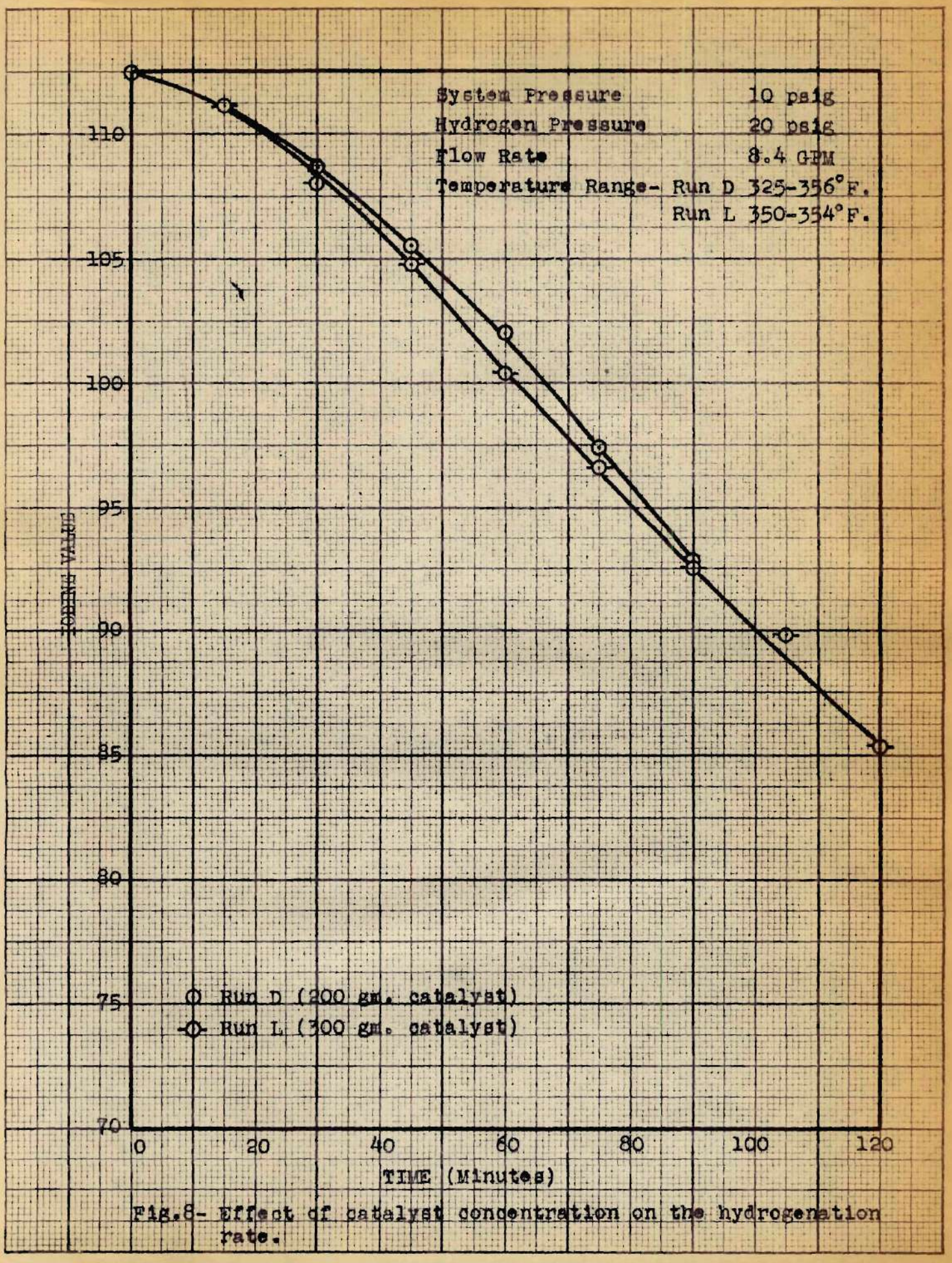


Fig.8- Effect of catalyst concentration on the hydrogenation rate.

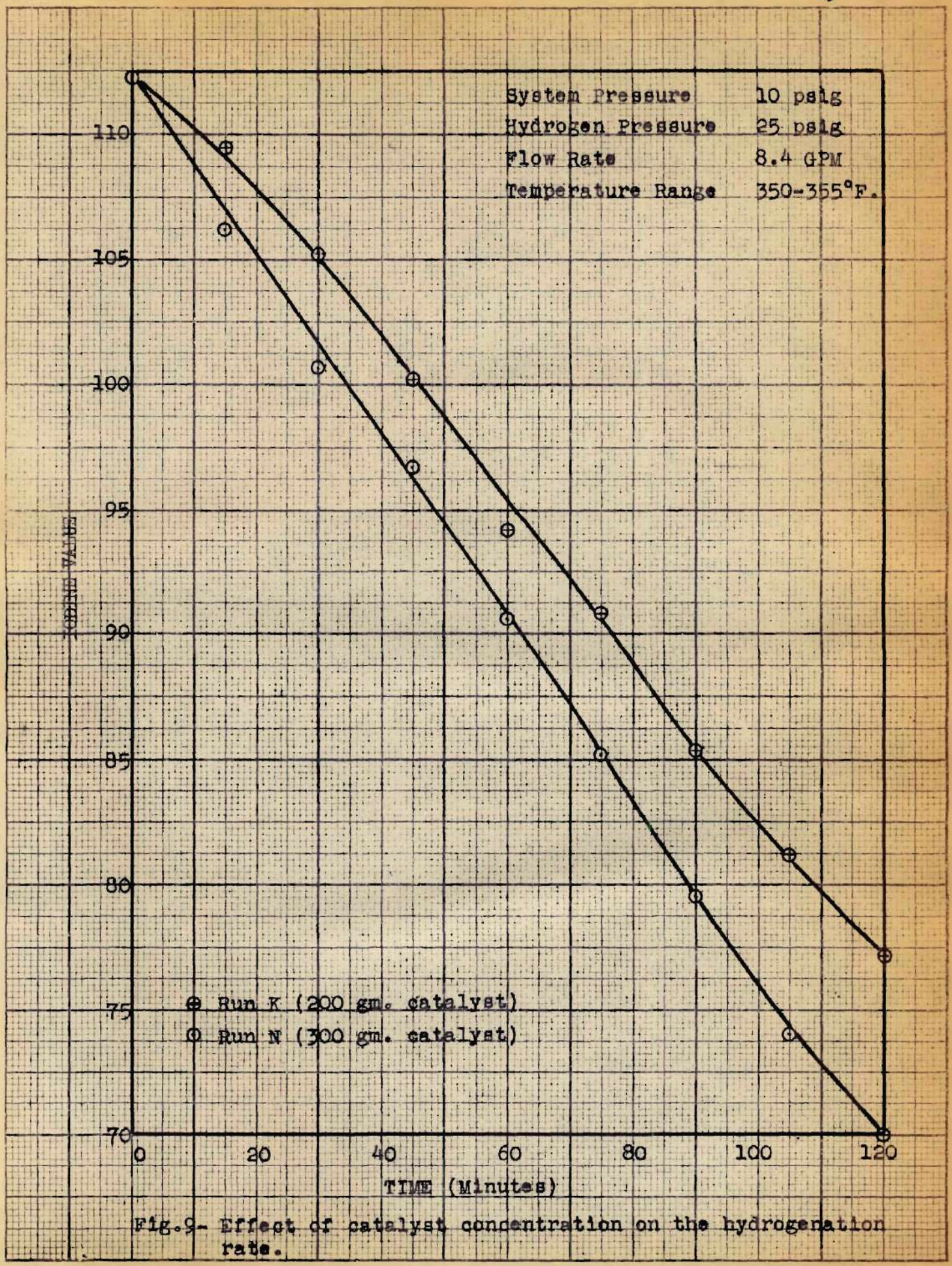


Fig. 9- Effect of catalyst concentration on the hydrogenation rate.

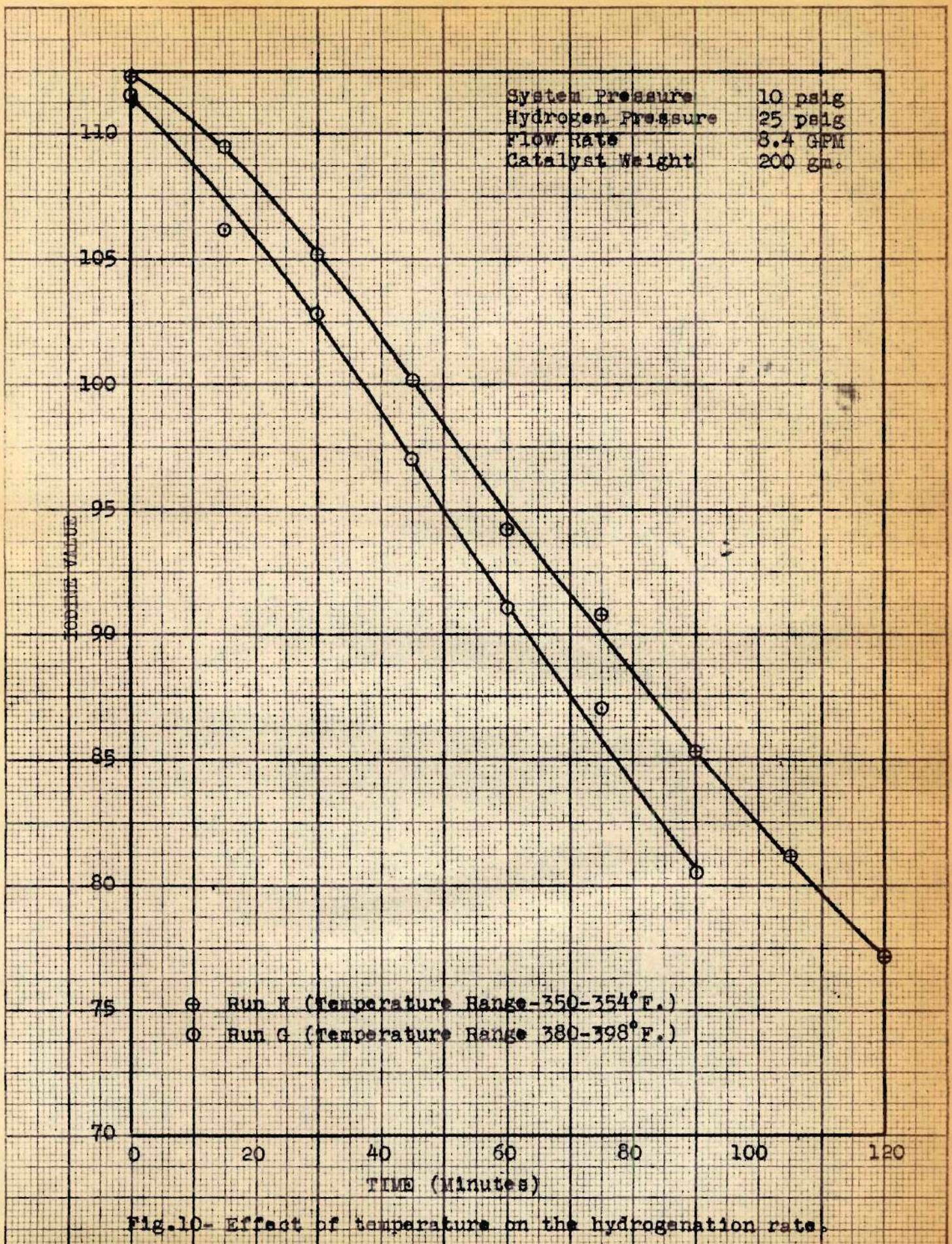
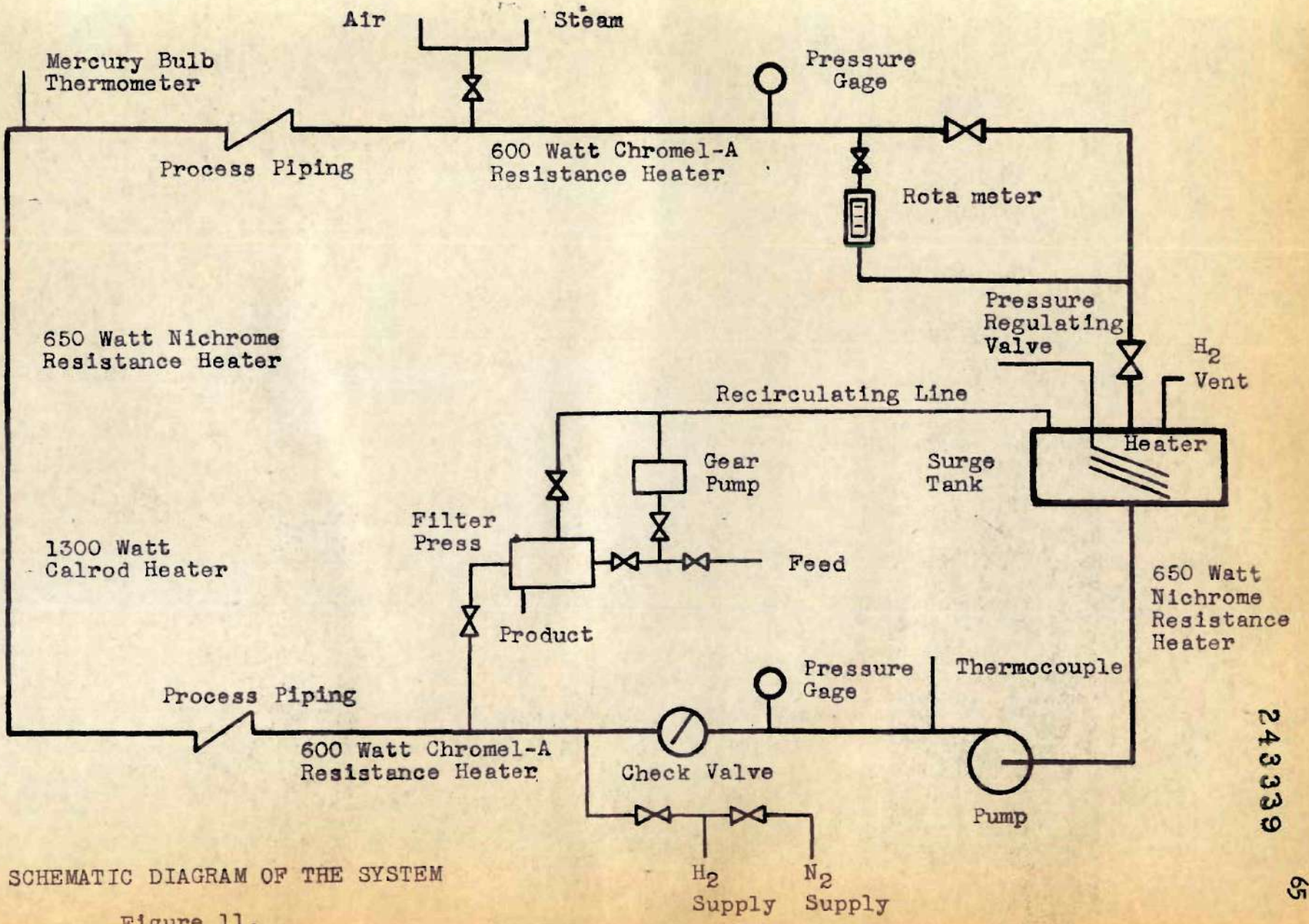


Fig.10- Effect of temperature on the hydrogenation rate.



SCHEMATIC DIAGRAM OF THE SYSTEM

Figure 11.